THE UNIVERSITY OF UTAH

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Technical Support on Potential Catalyst Systems Related to Preparation, Characterization and Evaluation of Shape Selective Deoxygenation Catalysts for Biomass Pyrolysis Products

Introduction

During the first twelve months of the NREL phase III project, work progressed in constructing and testing synthesis, extrusion and calcination equipment and in constructing the catalyst evaluation unit. Additional work was performed to prepare and characterize large-batch catalyst samples which have been delivered to NREL. An additional characterization technique was applied in the course of these studies to determine cation exchange capacity of the synthesized materials. The technique involved the

combination of TGA and tetramethylammonium decomposition. Furthermore, a catalyst evaluation unit was designed and fabricated and has been commissioned in a series of preliminary, non-catalytic experiments. The reader is referred to Memorandum NREL-24 First Year Draft Technical Report - October 1993 through October 1994 (NREL Subcontract Number ZAA-3-13433-01) for a detailed discussion of the progress on the individual Tasks summarized in this Memorandum.

TASK STATUS

Task 1: Prepare promising catalysts in an extrudate form containing a binder.

A method and the appropriate laboratory scale apparatus for extruding alumina-bound shape selective molecular sieve catalysts have been developed in the course of the Phase III program. The extruder was used to prepare a series of alumina bound catalysts for use in the NREL studies of deoxygenation catalysis for biomass pyrolysis products. The extrusion procedures have evolved to a point where reproducible extrudates can be routinely prepared. The following catalysts were synthesized and extruded with alumina and have been delivered to NREL: H/[Al,Fe]ZSM-5-P7; SAPO-11-P8; Cu,H/[Al]ZSM-5-P9; SAPO-11-P8; Alumina-:12; H/[Al]ZSM-5-P13;H/[Al]Z5M-5-P14; and H/[Al]ZSM-5-P15. These catalysts will be evaluated for oxygenate conversion and selectivity in the catalyst testing unit once it is available for routine operation.

Task 2: Modify previously identified promising catalysts.

A. Improve catalyst preparation by utilizing stirring during autoclave synthesis.

A major redesign of the stirrer-shaft seals was accomplished during this period which took advantage of the autogenesis pressure developed in the autoclave during synthesis to seal the shaft. The redeisnged seals functioned very well and all large-batch catalysts delivered to NREL were prepared in the stirred autoclave.

B. Develop reproducible procedures for catalyst calcination and steaming to investigate catalyst optimization.

A calciner was designed and fabricated for use in preparing the large-batch alumina-bound catalysts delivered to NREL. The calciner was also used to study catalyst calcination and activiation procedures to develop an appropriate calcination method which would minimize dealumination of the zeolite framework.

C. Investigate and optimize the effect of crystallite size on the activity of Co-exchanged ZSM-5.

Three synthesis variables were adjusted in an attempt produce small crystal ZSM-5. The changes included the following: (1) increase the template/silica ratio; 2) lower the nucleation temperature; and 3) increase the hydroxide concentration. The modifications led to the formation of smaller crystals; however, the change in crystallite size did not impact cobalt exchange since cobalt can be completely exchanged into ZSM-5 regardless of the crystal size.

Task 3: Prepare new potential catalysts.

The preparation of new potential catalysts has been delayed while the data generated in the NREL catalyst evaluation studies is reviewed by the NREL staff. Following the review and interpretation of the data the insights gained will be used to guide the selection of candidate catalysts for preparation.

A. Investigate olefin selectivity enhancement by synthesizing FAPSO-11 and ZSM-48.

Preparation of potential olefin selective catalysts, FAPSO-11, ZSM-48 and ZSM-23, will be done after the catalyst evaluation unit (see Task 5) is available for routine catalyst testing. The modification of small-batch catalyst preparation schemes to produce highly selective catalysts requires less than a one-week turnaround on catalyst evaluation studies so that significant progress can be made. Once small-batch preparation schemes have been fine-tuned to produce olefin selective catalysts large-batch catalyst preparations will be undertaken to provide catalyst samples for delivery to NREL.

B. Investigate enhanced activity catalysts by combining the advantages of Cu- and Co-containing ZSM-5 with the beneficial effects of structural iron.

These catalysts have not yet been synthesized on either a small-batch or large-batch scale.

Task 4: Characterize freshly prepared catalyst samples.

All alumina-bound catalysts delivered to NREL were subjected to standard characterization tests: α-activity test; ammonia temperature programmed

desorption; hexane or water adsorption; TGA; x-ray diffraction and scanning electron microscopy. An alternative to ammonia temperature programmed desorption has been developed to determine cation exchange capacity of the synthesized zeolites. The technique, thermal gravimetric analysis of tetramethylammonium decomposition, was specific for the determination of Brønsted acidity.

Task 5: Develop an alternative to the α-activity test to determine deoxygenation activity of catalyst samples.

The catalyst testing and evaluation unit was designed and construction was completed during this period. The system was fabricated as a modular apparatus: a system control and monitor module; a gas and liquid feed module and a reactor-product recovery module. Preliminary flow tests and calibration experiments have been completed. Several test runs have been conducted using methanol as the liquid feed and sand as an inert reaction packing.

Task 6: Characterize specific spent catalysts.

None of the Phase III catalysts samples forwarded to NREL for evaluation have been returned to the University of Utah for post-reaction testing and characterization. Selected spent catalysts will be returned to the University of Utah at the discretion of NREL for characterization during the Phase IIIA program.

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